New reference function for platinum-10% rhodium versus platinum (type S) thermocouples based on the ITS-90. Part II: Results and discussion.

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ABSTRACT

The Comité Consultatif de Thermométrie requested its Working Group 2 to collaborate with national laboratories in the production of new reference tables and functions for thermocouples based on the International Temperature Scale of 1990 (ITS-90). Pursuant to this recommendation, eight national laboratories have obtained new data on type S thermocouples obtained from several sources. The thermoelectric voltages of those thermocouples have been measured as a function of t_{90} in the range -50 °C to 1070 °C, with temperatures obtained from standard platinum resistance thermometers that were calibrated in accordance with the ITS-90 to 962 °C and extrapolated to 1070 °C. Also, in the range from 710 °C to 1065 °C, temperatures were measured with a radiation thermometer. In addition, the thermoelectric voltages of the thermocouples have been determined at various thermometric fixed points. From the results of these measurements, polynomials giving the thermoelectric voltage as a function of t_{90} have been developed, and new estimates for the temperature differences between the ITS-90 and the IPTS-68 in the range 630 °C to 1064 °C have been derived.

SUBJECT INDEX: Calibration methods, International Temperature Scale of 1990 (ITS-90), Noble metal thermocouple thermometers

INTRODUCTION

The adoption of the International Temperature Scale of 1990 (ITS-90) (1), which supersedes the International Practical Temperature Scale of 1968, amended edition of 1975 (IPTS-68) (2), requires that the reference functions and tables for the thermocouples incorporated in various national and international standards (3, 4, 5) be revised to give the electromotive force (*emf*) as a function of t_{90}. Mathematical conversions of the previous thermocouple functions (6) were performed at NIST using the temperature scale differences tabulated in Ref. 1, but they produced unsatisfactory results due to the slope discontinuity at t_{68} = 630.74 °C (7) that was inherent in the IPTS-68. Consequently, Working Group 2 of the Comité Consultatif de Thermométrie circulated a request (July 1990) to national laboratories inviting an international collaborative effort to generate new experimental data for Pt-10%Rh vs. Pt (type S) thermocouples. Pursuant to this request, eight national laboratories obtained new data for the determination of new reference functions and tables for the type S thermocouple based on the ITS-90. This part of the paper presents the results obtained from this international collaboration and gives the new reference and inverse functions. Data from seven of the participating laboratories were used for a new determination of (t_{90} - t_{68}) values over the range 630 °C to 1064 °C and the results are presented.

The experimental procedures, apparatuses, and materials used in obtaining the data were described in Part I of this paper. The *emf*-t_{90} relationships of type S thermocouples were measured at the eight laboratories using different thermocouples, different experimental procedures, and, of course, different apparatuses. Altogether, such measurements were obtained for 37 thermocouples acquired from several sources. At all the laboratories, measurements were made of the *emf* of the thermocouples as a function of t_{90} over the range 630 °C to 962 °C, with t_{90} being determined with high temperature standard platinum resistance thermometers (HTSPRTs), calibrated according to the ITS-90. Henceforth in this paper, this will be referred to as a comparison measurement. Similar measurements with standard platinum resistance thermometers (SPRTs) were conducted within the range -50 °C to 630 °C at SIPAI and NIST. At IMGC, temperatures from 710 °C to 1065 °C were measured also with an infrared pyrometer, while at NIST temperatures up to 1070 °C were measured with an HTSPRT. In addition, the thermocouples were calibrated at various thermometric fixed points as realized either in metal freezing-point cells or by the melting-wire method. The methods used for the measurements and the number of thermocouples tested at each laboratory are summarized in Part I (see Table I).

RESULTS AND DISCUSSION

Computation of $(t_{90} - t_{68})$ values

Since the type S thermocouple was the standard interpolating instrument on the IPTS-68 (2) in the range from t_{68} = 630.74 °C to t_{68} = 1064.43 °C, values of the temperature differences between the ITS-90 and the IPTS-68 in this range were derived from our *emf*-t_{90} measurements. On the IPTS-68, the temperature, t_{68}, determined from type S thermocouples, is defined by the relation

$$E = a + bt_{68} + ct_{68}^2 \,, \qquad (1)$$

where E is the *emf* when one of the junctions of the thermocouple is at 0 °C and the other is at t_{68}. The coefficients a, b, and c are calculated from values of E at t_{68} = 630.74 °C ± 0.2 °C, as determined by an SPRT, and at t_{68} = 961.93 °C and t_{68} = 1064.43 °C, the freezing points of Ag and Au, respectively. It should be noted that at these three temperatures, the adopted differences (1,7) for $(t_{90} - t_{68})$ are −0.125 °C, −0.15 °C, and −0.25 °C, respectively , and that the corresponding values of t_{90} at these points are 630.615 °C, 961.78 °C, and 1064.18 °C. We accepted the adopted differences between the scales at these temperatures in deriving the $(t_{90} - t_{68})$ values presented here.

The procedure for calculating $(t_{90} - t_{68})$ values from the *emf*-t_{90} data consisted of a three-step process. As a first step, the IPTS-68 quadratic for each thermocouple was determined. Next, for each of the measured values of *emf* within the range 630.615 °C to 1064.43 °C, the corresponding value of t_{68} was obtained from the IPTS-68 quadratic by iteration. The calculated values of t_{68} were then subtracted from the measured values of t_{90}. Such calculations were carried out for the 24 thermocouples (see Table I in Part I), whose calibrations included a measurement at the Au point.

The *emf* values at 630.615 °C, 961.78 °C, and 1064.18 °C for determining the IPTS-68 quadratic were obtained from the comparison and fixed-point data in the following ways. Values of *emf* at 630.615 °C and 961.78 °C were obtained for all 24 thermocouples from the HTSPRT-thermocouple comparison data by interpolation. For the 5 NIST thermocouples, *emf* values at 1064.18 °C were interpolated from the comparison data. Similarly, for the four thermocouples that were compared with an infrared pyrometer at IMGC, *emf* values were interpolated at 961.78 °C and 1064.18 °C from those comparison data. For the thermocouples that were measured at fixed points both before and after comparison with the HTSPRT, the mean of the *emf* values obtained before and after the comparison was computed at each fixed point, except for the two VSL thermocouples. Both of the VSL thermocouples, as discussed in Ref. 8, changed appreciably during the experiment, and the fixed-point data obtained prior to the comparison measurements differed substantially from the comparison data; hence, the initial fixed-point measurements were not used.

All of the thermocouples, except VSL-A, met the *emf* requirements for standard thermocouples on the IPTS-68 (see Eqs. (13), (14), (15) in Ref. 2) The values of *emf* for VSL-A did not satisfy Eq. (14) in Ref. 2.

Trial calculations of $(t_{90} - t_{68})$ values were made using various combinations of the *emf* values obtained from the comparison and fixed-point data to determine the IPTS-68 quadratic. It was clear that the best estimate for a particular thermocouple was realized by using data obtained in the same apparatus. For 15 thermocouples it was necessary, however, to use the fixed-point measurement at 1064.18 °C. In this instance we believe that better continuity in the results can be realized by using the mean of the fixed-point and comparison values at 961.78 °C, together with the *emf* value at 630.615 °C interpolated from the comparison data, to determine the IPTS-68 quadratics. Hence, the quadratics used to compute the $(t_{90} - t_{68})$ values presented here for those thermocouples, as well as for the four IMGC thermocouples that were compared with an HTSPRT, were determined in this manner. A second set of quadratics was calculated for the IMGC thermocouples using the *emf* values at 1064.18 °C and 961.78 °C interpolated from the infrared pyrometer comparison data and *emf* values at 630.615 °C obtained by computing the means of the HTSPRT-comparison and fixed-point (Sb). values. For the NIST thermocouples the IPTS-68 quadratics were determined by using the *emf* values interpolated from the comparison data at all three temperatures.

Because of chemical and physical inhomogeneities in the thermocouples and the different temperature gradients that existed in the comparison and fixed-point apparatuses, a given thermocouple was likely to produce a different value of *emf* at the same temperature in the two apparatuses. Analysis showed that at 961.78 °C, the difference between the *emf* value interpolated from the comparison data and the value obtained from fixed-point measurements was less than the equivalent of 0.1 °C for 19 of the 24 thermocouples. The difference between the comparison and fixed-point values at 1064.18 °C was less than 55 m°C for 8 of the 9 NIST and IMGC thermocouples. Such surprisingly close agreement was achieved, we believe, because the same furnace was used at NIST for the fixed-point and comparison measurements, while the blackbody comparator used at IMGC was designed (8) to have very nearly the same immersion conditions as the fixed-point apparatus.

The $(t_{90} - t_{68})$ values calculated from the IMGC, KRISS, NIST, NPL, NRLM, VNIIM, and VSL thermocouple data are shown in Figs. 1, 2, 3, 4, 5, 6, and 7, respectively. The previously published values (CIPM, see Ref. 1) for the temperature differences are shown for comparison. Statistical analysis of the $(t_{90} - t_{68})$ values was performed using iteratively reweighted least squares regression to obtain a consensus model for the difference between the two temperature scales and is described in another paper at this Symposium (17). The 5th degree polynomial which describes this consensus model for $(t_{90} - t_{68})$ is

$$\begin{aligned} \Delta t\,(t_{90}) = \quad & (7.8687209 \times 10^{1}) \\ & -(4.7135991 \times 10^{-1})t_{90} \\ & (1.0954715 \times 10^{-3})t_{90}^2 \\ & -(1.2357884 \times 10^{-6})t_{90}^3 \\ & (6.7736583 \times 10^{-10})t_{90}^4 \\ & -(1.4458081 \times 10^{-13})t_{90}^5 \end{aligned} \qquad (2)$$

Figure 8 shows the $(t_{90} - t_{68})$ values computed from this polynomial, the values calculated from type S thermocouple data of the seven laboratories, and the previously published (CIPM) values (1).

Thermocouple reference functions

The new reference function giving the *emf* as a function of t_{90} over the range from −50 °C to 1064.18 °C is based upon the experimental data for NIST thermocouple S5. The rationale for this choice and the analysis of the data are given in Ref. 17. An 8th degree polynomial was fitted to the *emf*-t_{90} data for thermocouple S5 by the method of least squares. The residual standard deviation was 0.063 μV with 436 degrees of freedom. The polynomial was then adjusted quadratically, as described in Ref. 17, to obtain the reference function. As a consequence of this adjustment, the reference function gives the same value of *emf* at the freezing point of gold as the previous reference function (6), after the latter was corrected to account for the 1 January 1990 change in the volt (18).

Above 1064.18 °C, the new reference functions are based upon mathematical conversions of the IPTS-68 based reference functions (6). The previous functions consist of two cubics which join at t_{68}=1665 °C. The use of two functions was necessary to accommodate the rapid decrease of the Seebeck coefficient above 1700 °C. Direct substitution of $t_{68} = t_{90} - \Delta t$ in the cubics, where Δt is given by Eq. (42) in Ref. 19, produced two 6th degree polynomials that give the *emf* as a function of t_{90}. The coefficients of both polynomials were multiplied by 0.999990736 to account for the change in the volt. These polynomials were then modified to obtain the reference functions as follows.

The 6th degree polynomial for the range 1064.18 °C to 1664.5 °C was truncated to a 4th degree polynomial. The coefficients of the 4th degree polynomial were then adjusted to obtain a polynomial that produces the same values of *emf* (E) and dE/dt_{90} at 1064.18 °C as the reference function of the preceding range and the same values of E and dE/dt_{90} at 1664.5 °C as the 6th degree polynomial before it was truncated. The resulting bias in the adjusted 4th degree polynomial relative to the 6th degree polynomial is ≤0.047 μV, in absolute terms. The adjusted 4th degree polynomial is used as the reference function in this range.

It should be noted that the previous reference function in the range above 1664.5 °C was based on t_{68} = 1767.6 °C (11) for the freezing point of Pt. More recent determinations of the Pt freezing-point temperature have resulted in a recommended value (20) of t_{68} = 1768.7 °C for this point.

The corresponding value of t_{90}, according to Eq. (42) in Ref. 19, is 1768.117 °C. Hence, in order for the new and old reference functions to give the same values of E at the freezing point of Pt, a corrective function was added in this range. First, the 6th degree polynomial for this range was truncated to a 4th degree polynomial, thereby incurring a bias of ≤0.022 μV. Then a cubic correction was made so that the resulting 4th degree polynomial produces the same values of E, dE/dt_{90}, and d^2E/dt_{90}^2 at 1664.5 °C as the reference function of the preceding range, and it also gives the same value of E at 1768.117 °C that the IPTS-68 based cubic gives at t_{68} = 1767.6 °C, after the latter is corrected to account for the change in the volt.

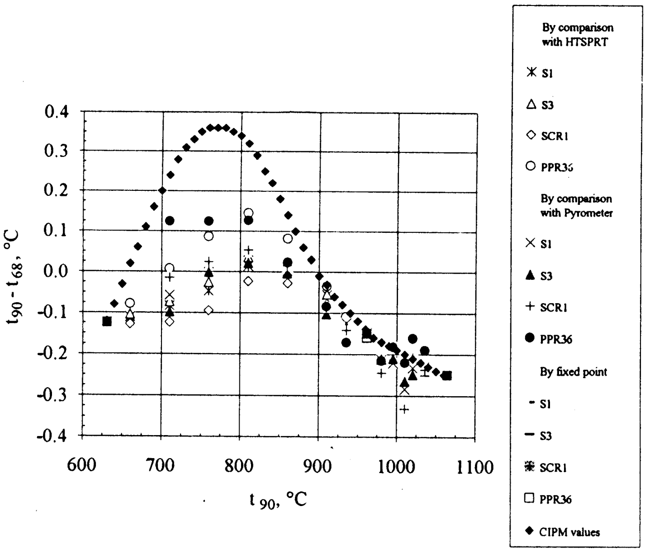

Figure 1. Values of t_{90} - t_{68} computed from IMGC type S thermocouple data compared with previously published CIPM values.

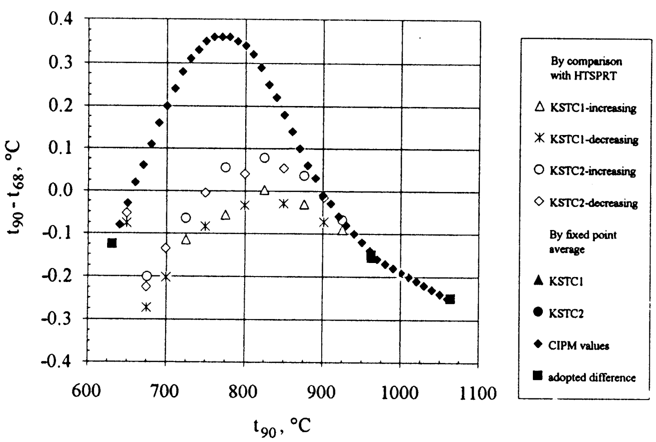

Figure 2. Values of t_{90} - t_{68} computed from KRISS type S thermocouple data compared with previously published CIPM values.

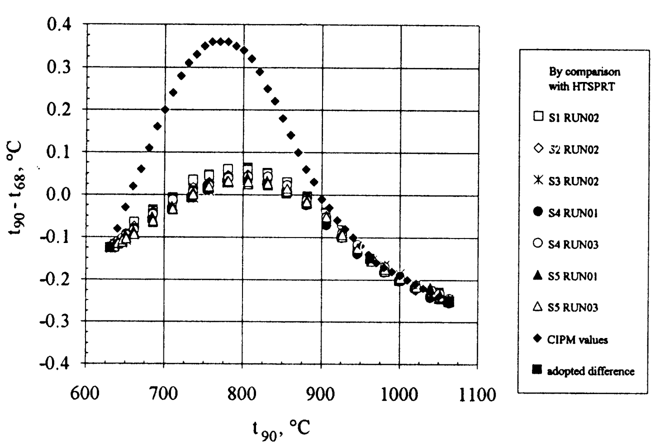

Figure 3. Values of t_{90} - t_{68} computed from NIST type S thermocouple data compared with previously published CIPM values.

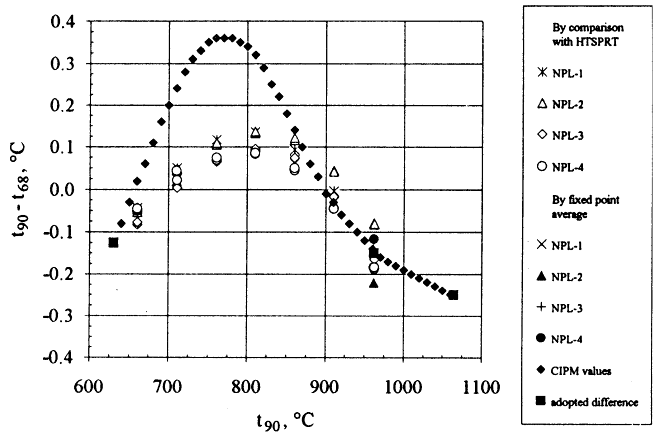

Figure 4. Values of t_{90} - t_{68} computed from NPL type S thermocouple data compared with previously published CIPM values.

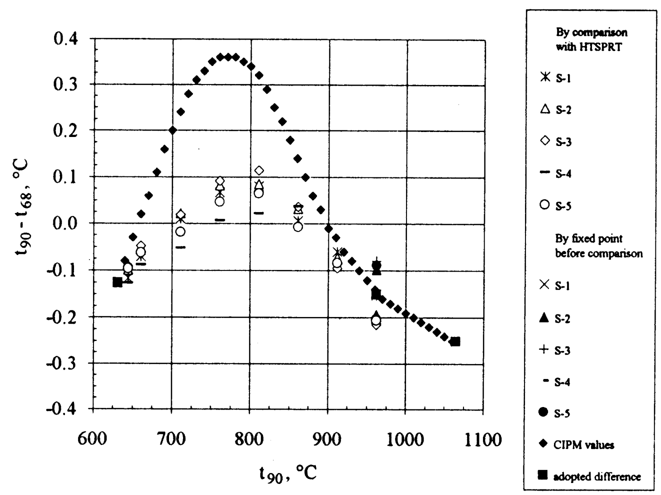

Figure 5. Values of t_{90} - t_{68} computed from NRLM type S thermocouple data compared with previously published CIPM values.

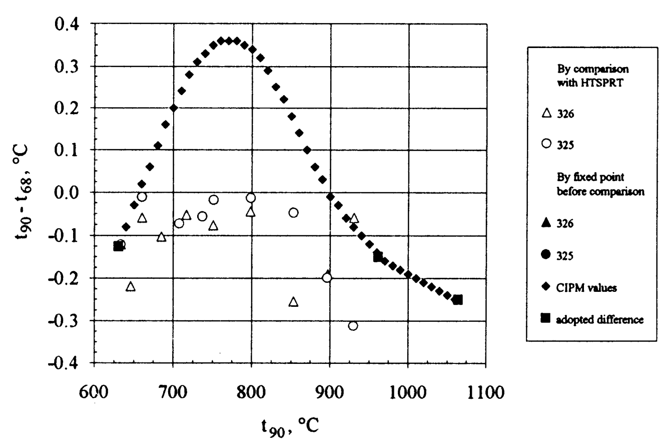

Figure 6. Values of t_{90} - t_{68} computed from VNIIM type S thermocouple data compared with previously published CIPM values.

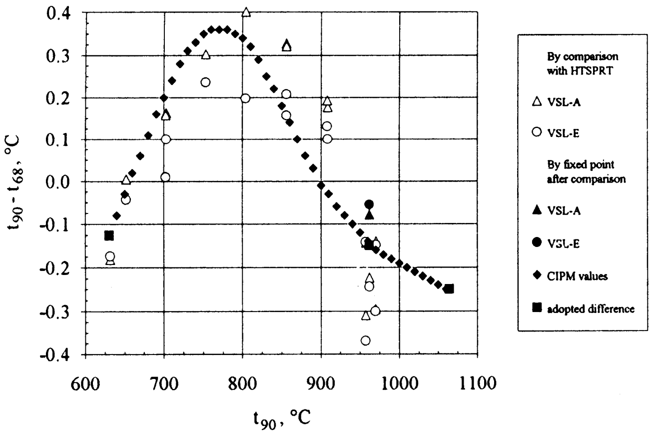

Figure 7. Values of t_{90} - t_{68} computed from VSL type S thermocouple data compared with previously published CIPM values.

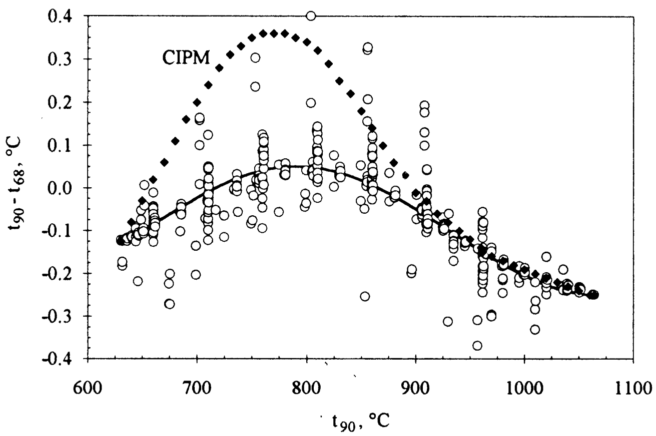

Figure 8. Values of t_{90} - t_{68} computed from type S thermocouple data (open circles) from all of the seven national laboratories compared with previously published CIPM values (solid diamonds). The line represents the 5th degree polynomial fitted to the data by iteratively reweighted least-squares regression.

The new reference functions for the type S thermocouples are of the form:

$$E = \sum_{i=0}^{n} a_i \, (t_{90})^i \,, \tag{3}$$

where t_{90} is in degrees Celsius and E is in microvolts. The coefficients of Eq. (3) for the various temperature ranges are given in Table I.

Table I. Coefficients of the reference functions for type S thermocouples for the indicated temperature ranges.

−50 °C to 1064.18 °C		1064.18 °C to 1664.5 °C		1664.5 °C to 1768.1 °C	
a_1	5.40313308631	a_0	$1.32900444085 \times 10^{3}$	a_0	$1.46628232636 \times 10^{5}$
a_2	$1.25934289740 \times 10^{-2}$	a_1	3.34509311344	a_1	$-2.58430516752 \times 10^{2}$
a_3	$-2.32477968689 \times 10^{-5}$	a_2	$6.54805192818 \times 10^{-3}$	a_2	$1.63693574641 \times 10^{-1}$
a_4	$3.22028823036 \times 10^{-8}$	a_3	$-1.64856259209 \times 10^{-6}$	a_3	$-3.30439046987 \times 10^{-5}$
a_5	$-3.31465196389 \times 10^{-11}$	a_4	$1.29989605174 \times 10^{-11}$	a_4	$-9.43223690612 \times 10^{-12}$
a_6	$2.55744251786 \times 10^{-14}$				
a_7	$-1.25068871393 \times 10^{-17}$				
a_8	$2.71443176145 \times 10^{-21}$				

Values of E and the first and second derivatives of E with respect to t_{90} computed from the reference functions (see Eq. (3) and Table I) at selected values of t_{90} are given in Table II.

Table II. Values of E and the first and second derivatives of E with respect to t_{90} computed from equation (3) at selected values of t_{90}.

t_{90}, °C	E, µV	dE/dt_{90}, µV/°C	d^2E/dt_{90}^2, nV/°C²
-38.8344	-189.40	4.312	31.23
0.000	0.00	5.403	25.19
0.01	0.05	5.403	25.19
29.7646	171.39	6.094	21.36
156.5985	1082.27	8.045	10.69
231.928	1715.00	8.711	7.24
419.527	3446.89	9.638	3.50
630.615	5552.64	10.303	3.16
660.323	5860.13	10.398	3.23
961.78	9148.38	11.418	3.22
1064.18	10334.20	11.743	3.27
1084.62	10574.80	11.798	2.55
1664.5	17535.96	11.681	-2.94
1768.1	18693.54	10.311	-23.52

Figure 9 shows the *emf* difference between the new ITS-90 based reference functions and the IPTS-68 based reference functions. The IPTS-68 based reference functions were converted to the ITS-90 and corrected for the change in the volt. The conversion of the IPTS-68 based reference function in the range 630.615 °C to 1064.18 °C is based on Eq. (2). The dashed line in the figure labelled +1 °C is the Seebeck coefficient as a function of t_{90}.

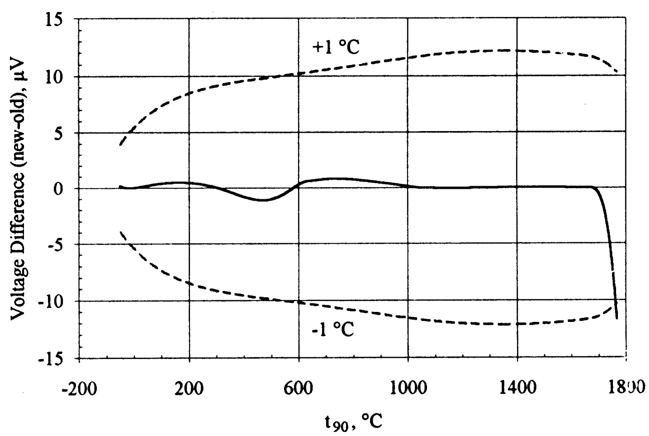

Figure 9. Differences between the new ITS-90 reference functions and the old IPTS-68 reference functions for type S thermocouples. The values of the old type S reference functions are adjusted to the ITS-90 and corrected for the change in the volt. The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

The deviations of the IMGC, KRISS, NIST, NPL, NRLM, SIPAI, VNIIM, and VSL thermocouple data from the new reference function are shown in Figs. 10, 11, 12, 13, 14, 15, 16, and 17, respectively. The dashed lines in the figures, which indicate an *emf* deviation equivalent to ±1 °C, represent the Class I manufacturing tolerance for type S thermocouples as given in IEC standard 584-2 (21). Twenty eight of the 37 thermocouples used in this effort satisfy the Class I tolerance.

Since the reference functions given above are not well suited for calculating values of temperature from values of *emf*, a set of inverse functions, based on the ITS-90, is included here for that purpose. These inverse functions give values of temperature that agree with values obtained from the respective reference function to at least ±0.02 °C. The inverse functions are of the form:

$$t_{90} = \sum_{i=0}^{n} b_i \, (E)^i \,, \tag{4}$$

where t_{90} is in degrees Celsius and E is given in microvolts. The coefficients of Eq. (4) for various temperature and *emf* ranges are given in Table III.

Table III. Coefficients of inverse functions for the type S thermocouples for the indicated temperature and *emf* ranges.

−50 °C to 250 °C −236 µV to 1874 µV		250 °C to 1200 °C 1874 µV to 11951 µV	
		b_0	$1.291507177 \times 10^{1}$
b_1	$1.84949460 \times 10^{-1}$	b_1	$1.466298863 \times 10^{-1}$
b_2	$-8.00504062 \times 10^{-5}$	b_2	$-1.534713402 \times 10^{-5}$
b_3	$1.02237430 \times 10^{-7}$	b_3	$3.145945973 \times 10^{-9}$
b_4	$-1.52248592 \times 10^{-10}$	b_4	$-4.163257839 \times 10^{-13}$
b_5	$1.88821343 \times 10^{-13}$	b_5	$3.187963771 \times 10^{-17}$
b_6	$-1.59085941 \times 10^{-16}$	b_6	$-1.291637500 \times 10^{-21}$
b_7	$8.23027880 \times 10^{-20}$	b_7	$2.183475087 \times 10^{-26}$
b_8	$-2.34181944 \times 10^{-23}$	b_8	$-1.447379511 \times 10^{-31}$
b_9	$2.79786260 \times 10^{-27}$	b_9	$8.211272125 \times 10^{-36}$

1064 °C to 1664.5 °C 10332 µV to 17536 µV		1664.5 °C to 1768.1 °C 17536 µV to 18694 µV	
b_0	$-8.087801117 \times 10^{1}$	b_0	$5.333875126 \times 10^{4}$
b_1	$1.621573104 \times 10^{-1}$	b_1	$-1.235892298 \times 10^{1}$
b_2	$-8.536869453 \times 10^{-6}$	b_2	$1.092657613 \times 10^{-3}$
b_3	$4.719686976 \times 10^{-10}$	b_3	$-4.265693686 \times 10^{-8}$
b_4	$-1.441693666 \times 10^{-14}$	b_4	$6.247205420 \times 10^{-13}$
b_5	$2.081618890 \times 10^{-19}$		

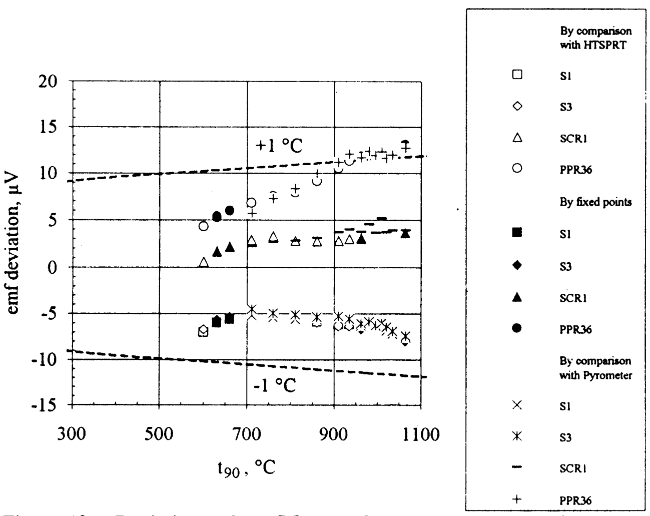

Figure 10. Deviations of IMGC type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

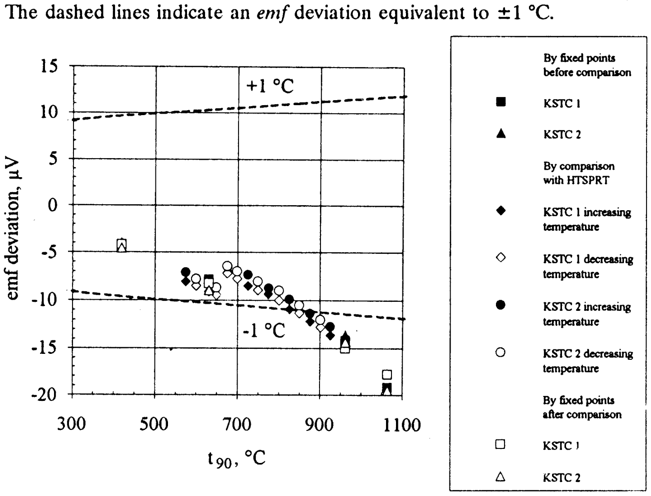

Figure 11. Deviations of KRISS type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

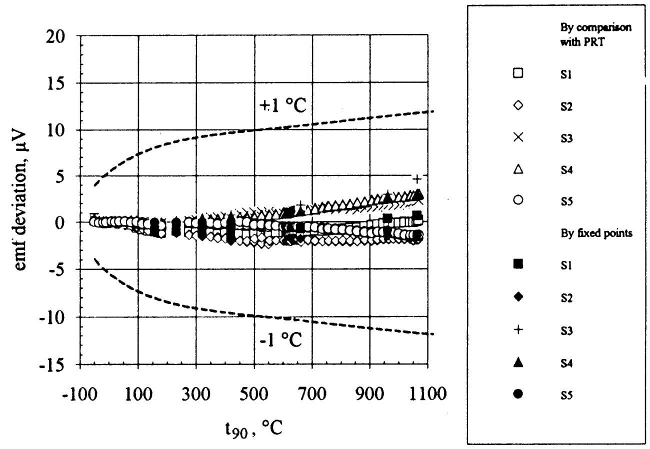

Figure 12. Deviations of NIST type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

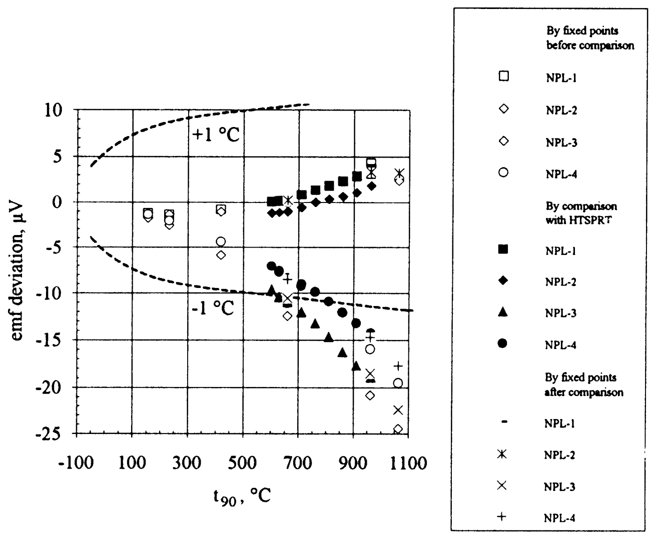

Figure 13. Deviations of NPL type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

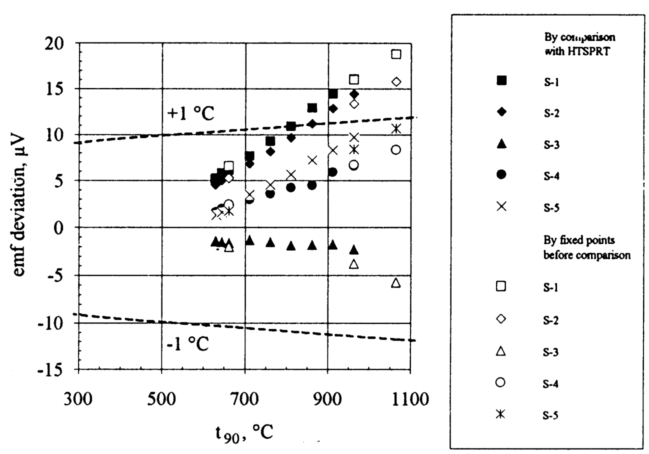

Figure 14. Deviations of NRLM type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

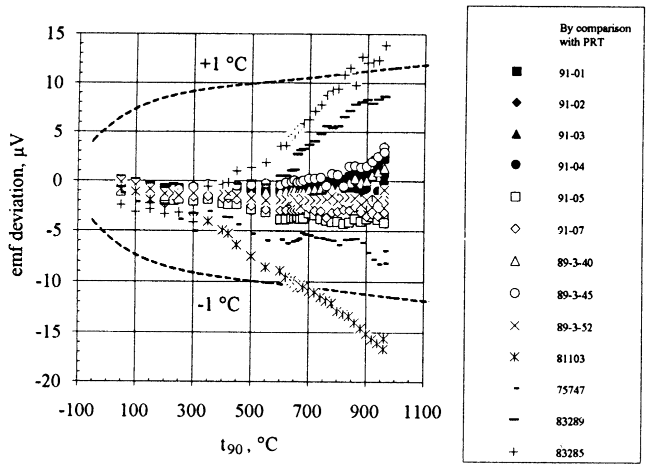

Figure 15. Deviations of SIPAI type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

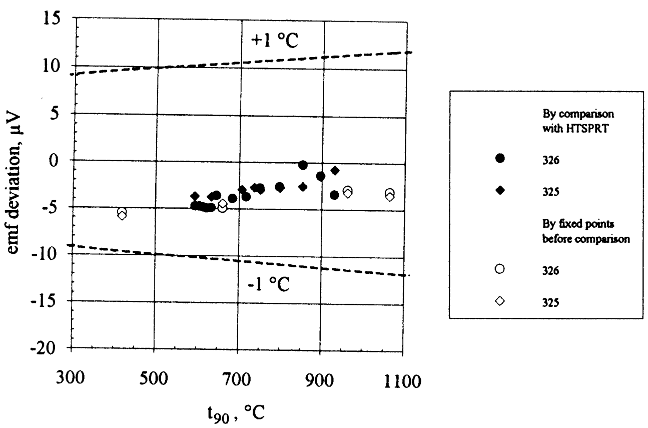

Figure 16. Deviations of VNIIM type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

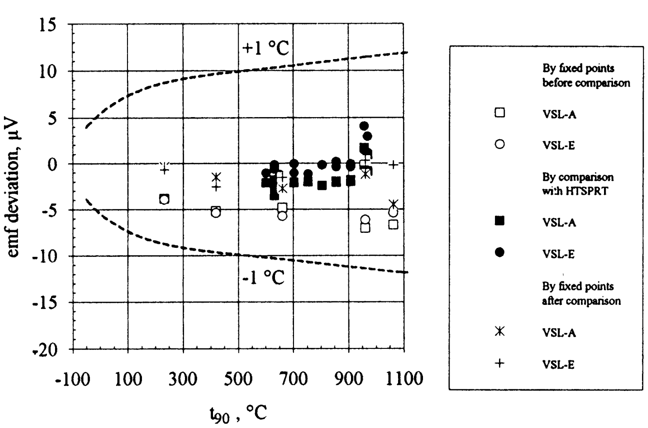

Figure 17. Deviations of VSL type S thermocouple data from the reference function (deviation = measured *emf* values - reference function). The dashed lines indicate an *emf* deviation equivalent to ±1 °C.

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